

# Computational Physics of Materials

## Lecture 5: Density Functional Theory I

2:00 - 3:15 M, W

Daniels 331

<http://courses.ncsu.edu/py615/lec/601/>

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# Towards Density Functional Theory

- The fundamental tenet of Density Functional Theory is that the complicated many-body electronic wavefunction  $\Psi$  can be substituted by a much simpler quantity, that is the electronic density

$$n(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \frac{\int d^3r_2 d^3r_3 \cdots d^3r_N \sum_s |\Psi(\{\mathbf{r}\})|^2}{\int d^3r_1 d^3r_2 \cdots d^3r_N |\Psi(\{\mathbf{r}\})|^2}$$

- This means that a scalar function of position,  $n(\mathbf{r})$ , determines all the information in the many-body wavefunction for the ground state and in principle, for all excited states
- $n(\mathbf{r})$  is a simple non-negative function subject to the particle conservation sum rule

$$\int n(\mathbf{r}) d^3r = N$$

where  $N$  is the total number of electrons in the system

# Definitions

**Function:** a prescription which maps one or more numbers to another number:

$$y = f(x) = x^2$$

**Operator:** a prescription which maps a function onto another function:

$$O = \frac{\partial^2}{\partial x^2} \text{ so that } Of(x) = \frac{\partial^2}{\partial x^2} f(x)$$

**Functional:** A functional takes a function as input and gives a number as output:

$$F[f(x)] = y$$

Here  $f(x)$  is a function and  $y$  is a number.

An example is the functional to integrate  $x$  from  $-\infty$  to  $\infty$ :

$$F[f(x)] = \int_{-\infty}^{\infty} f(x) dx$$

# Towards Density Functional Theory

- Density Functional Theory (DFT) is based on ideas that were around since the early 1920's: Thomas-Fermi theory of electronic structure of atoms (1927)
  - Electrons are distributed uniformly in the 6-dimensional space (3 spatial coordinates x 2 spin coordinates) at the rate of 2 electrons per  $h^3$  of volume
  - There is an effective potential fixed by the nuclear charges and the electron density itself
- Energy functional for an atom in terms of the electron density alone

$$E_{TF} [n(\mathbf{r})] = \underbrace{C_1 \int n^{5/3}(\mathbf{r}) d^3r}_{\text{Kinetic energy}} + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r + \underbrace{C_2 \int n^{4/3}(\mathbf{r}) d^3r}_{\text{Local exchange}} + \frac{1}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

- Need approximate terms for kinetic energy and electronic exchange - no correlations
- Kinetic energy of the system electrons is approximated as an explicit functional of the density, idealized as non-interacting electrons in a homogeneous gas with density equal to the local density at any given point.
- Local exchange term later added by Dirac (still used today)

# Thomas-Fermi method

- The ground state density and energy can be found by minimizing the functional  $E[n]$  for all possible  $n(\mathbf{r})$  subject to the constraint on the total number of electrons

$$\int d^3r n(\mathbf{r}) = N$$

- Using the method of Lagrange multipliers, the solution can be found by an unconstrained minimization of the functional

$$\Omega_{TF}[n] = E_{TF}[n] - \mu \left[ \int d^3r n(\mathbf{r}) - N \right]$$

where  $\mu$  (Lagrange multiplier) is the Fermi energy

- For small variations of the density  $\delta n(\mathbf{r})$ , the condition for a stationary point leads to the following relation between density and total potential

$$\frac{1}{2}(3\pi^2)^{2/3} n(\mathbf{r})^{2/3} + V(\mathbf{r}) - \mu = 0$$

with  $V(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_x(\mathbf{r})$

- Only one equation for the density! remarkably simpler than the full many-body Schroedinger equation with  $3N$  degrees of freedom for  $N$  electrons

# The Hohenberg-Kohn theorems

- The revolutionary approach of Hohenberg and Kohn in 1964 was to formulate DFT as an **exact theory of a many-body system**
- The formulation applies to any system of interacting particles in an external potential  $V_{\text{ext}}(\mathbf{r})$ , including any problem of electrons and fixed nuclei, where the hamiltonian can be written

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Foundation of Density Functional Theory is in the celebrated Hohenberg and Kohn theorems

# Hohenberg-Kohn theorems

- DFT is based upon two theorems:
  - Theorem 1: For any system of electrons in an external potential  $V_{\text{ext}}(\mathbf{r})$ , that potential is determined uniquely, except for a constant, by the ground state density  $n_0(\mathbf{r})$
  - Corollary 1: Since the Hamiltonian is thus fully determined it follows that the many-body wavefunction is determined. Therefore, all properties of the system are completely determined given only the ground state density  $n_0(\mathbf{r})$
  - Theorem 2: A universal functional of the energy  $E[n]$  can be defined in terms of the density  $n(\mathbf{r})$ , valid for any external potential  $V_{\text{ext}}(\mathbf{r})$ . For any particular  $V_{\text{ext}}$  the exact ground state of the system is determined by the global minimum value of this functional
  - Corollary 2: The functional  $E[n]$  alone is sufficient to determine the ground state energy and density. In general, excited states have to be determined by other means.
  - The exact functionals are unknown and must be very complicated!

# Hohenberg-Kohn theorems

- Proofs of H-K theorems are exceedingly simple, and both based on a simple *reduction ad absurdum* argument
- Proof of Theorem 1: suppose there were two different external potentials  $V_{\text{ext}}^1$  and  $V_{\text{ext}}^2$  with same ground state density,  $n(\mathbf{r})$ .

The two potentials lead to two different Hamiltonians with different wavefunctions, that are hypothesized to lead to the same density. Then:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle$$

which leads to

$$E^{(1)} < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle = E^{(2)} + \int d^3r \{V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r})\}n(\mathbf{r})$$

But changing the labelling we can equally say that

$$E^{(2)} < E^{(1)} + \int d^3r \{V_{\text{ext}}^{(2)}(\mathbf{r}) - V_{\text{ext}}^{(1)}(\mathbf{r})\}n(\mathbf{r})$$

Summing the above expression we get the absurd result

$$E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)}$$

# Hohenberg-Kohn theorems

- There cannot be two different external potentials differing by more than a constant which give rise to the same non-degenerate ground state charge density.
  - The density uniquely determines the external potential to within a constant.
  - Then the wavefunction of any state is determined by solving the Schrodinger equation with this Hamiltonian.
  - Among all the solutions which are consistent with the given density, the unique ground state wavefunction is the one that has the lowest energy.
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- BUT: we are still left with the problem of solving the many-body problem in the presence of  $V_{\text{ext}}(\mathbf{r})$
  - EXAMPLE: electrons and nuclei - the electron density uniquely determines the positions and types of nuclei, which can easily be proven from elementary quantum mechanics, but we still are faced with the original problem of many interacting electrons moving in the potential due to the nuclei

# Hohenberg-Kohn theorems

- Theorem 2 gives us a first step towards an operative way to solve the problem
- Theorem 2 can be proved in a very similar way, and the demonstration leads to a general expression for the universal functional of the density in DFT

$$\begin{aligned} E_{HK}[n] &= T[n] + E_{\text{int}}[n] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\text{II}} \\ &\equiv F_{HK}[n] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\text{II}} \end{aligned}$$

- $F_{HK}[n]$  is a universal functional of the density that determines all the many-body properties of the system

$$F_{HK}[n] = T[n] + E_{\text{int}}[n]$$

- PROBLEM: we do not know what is this functional!

We only know that:

- is a functional of the density alone
- is independent on the external potential (thus its universality)
- It follows that if the functional  $F_{HK}[n]$  were known, then by minimizing the total energy of the system with respect to variations in the density function  $n(\mathbf{r})$ , one would find the exact ground state density and energy.

# Hohenberg-Kohn theorems

- The original proof of Hohenberg-Kohn is restricted to densities  $n(\mathbf{r})$  that are ground state densities of the electron hamiltonian with some external potential  $V_{\text{ext}}$
- The “V-representability” problem - leads to alternative definitions of the Density Functional (Levy-Lieb):
  - extends the range of definition of the functional in a way that is formally more tractable and clarifies its physical meaning
  - provides an in-principle way to determine the exact functional
  - leads to the same ground state density and energy at the minimum as in the Hohenberg-Kohn analysis

$$\begin{array}{ccc} V_{\text{ext}}(\mathbf{r}) & \xLeftrightarrow{\text{HK}} & n_0(\mathbf{r}) \\ \Downarrow & & \Uparrow \\ \Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) \end{array}$$

# Hohenberg-Kohn theorems

- two-step minimization procedure beginning with the usual general expression for the energy in terms of the many-body wavefunction first considering the energy only for the class of many-body wavefunctions  $\Psi$  that have the same density  $n(\mathbf{r})$

$$E = \langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{int} | \Psi \rangle + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r})$$

- Then, one can define a unique lowest energy for that given density by minimizing the above expression

$$\begin{aligned} E_{LL}[n] &= \min_{\Psi \rightarrow n(\mathbf{r})} [\langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{int} | \Psi \rangle] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{II} \\ &\equiv F_{LL}[n] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{II}, \end{aligned}$$

- This leads to the definition of the Levy-Lieb functional

$$F_{LL}[n] = \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{int} | \Psi \rangle$$

that is manifestly a functional of the density, and the ground state can be found by minimizing  $E_{LL}$ .

# Hohenberg-Kohn theorems

- LL is much more than a restatement of HK, since it provides an operational definition: the minimum of the sum of kinetic plus interaction energies for all possible wavefunctions having the given density  $n(\mathbf{r})$
- the LL functional is defined for any density  $n(\mathbf{r})$  derivable from a wavefunction  $\Psi_N$  for  $N$  electrons. This is termed “ $N$ -representability” and the existence of such a wavefunction  $\Psi_N$  for any density satisfying simple conditions is known
- In contrast, the Hohenberg-Kohn functional is defined only for densities that can be generated by some external potential; this is called “ $V$ -representability” and the conditions for such densities are not known in general
- Most important: At the minimum of the total energy of the system in a given external potential, the Levy-Leib functional  $F_{LL}[n]$  must equal the Hohenberg-Kohn functional  $F_{HK}[n]$
- Still: no way has been given to find the functional other than the original definition in terms of many-body wavefunctions. However, the dependence of the functional upon the kinetic and potential energies of the full, correlated many-body wavefunction points the way toward constructing approximate functionals that are of great utility in practical calculations and in understanding the effects of exchange and correlation among the electrons.

# Hohenberg-Kohn extensions

- Hohenberg-Kohn theorems can be generalized to several types of particles
- special role of the density and the external potential in the Hohenberg-Kohn theorems is that these quantities enter the total energy explicitly only through the simple bilinear integral term

$$\int d^3r V_{ext}(\mathbf{r})n(\mathbf{r})$$

- If there are other terms in the Hamiltonian having this form, then each such pair of external potential and particle density will obey a Hohenberg-Kohn theorem
- For example, Spin Density Functional Theory: Zeeman term that is different for spin up and spin down fermions in external magnetic fields
- All argument above can be generalized to include two types of densities, the particle density and the spin density

$$n_{total}(\mathbf{r}) = n(\mathbf{r}, \sigma = \uparrow) + n(\mathbf{r}, \sigma = \downarrow)$$

$$s(\mathbf{r}) = n(\mathbf{r}, \sigma = \uparrow) - n(\mathbf{r}, \sigma = \downarrow)$$

with a density functional

$$E = E_{HK}[n_{total}, s] \equiv E'_{HK}[n]$$

- In absence of magnetic fields, the solution can still be polarized (as in unrestricted Hartree-Fock theory)

# Hohenberg-Kohn extensions

- Extension to finite temperature functionals (Mermin)
- For each of the conclusions of Hohenberg and Kohn for the ground state, there exists a corresponding argument for a system in thermal equilibrium
- not only the energy, but also the entropy, specific heat, etc., are functionals of the equilibrium density!
- Problem: difficult to construct useful, approximate functionals for the entropy (which involves sums over excited states) than for the ground state energy
- Possible to generalize to other ensembles which are useful for aspects such as defining a functional of electron number as a continuous variable (in H-K,  $N$  is fixed), that becomes very useful for metallic systems
- Hohenberg-Kohn theorems assumed that the Hamiltonian is time reversal invariant. In a magnetic field, one needs to add a vector potential term in the Hamiltonian, so that the functional depends on both the density and the current density: Current Density Functional Theory

# Hohenberg-Kohn extensions

- Time Dependent Density Functional Theory: given the initial wavefunction at one time, the evolution at all later times is a unique functional of the time-dependent density
- Simple proofs, on the same spirit as the original HK proofs: formal step is constructing a density functional theory for excitations.
- Very important issue: Electric fields and polarizations
- In infinite space, the potential due to an electric field  $V(x) = Ex$  is unbounded; there is no lower bound to the energy and therefore there is no ground state
- if the ground state does not exist, the Hohenberg-Kohn theorems on the ground state do not apply
- Subtle problem that can be solved only if one applies constraints within which there is a stable ground state: for example, in a molecule (finite system) the constraint is that electrons have to remain near the molecule also in the presence of an external electric field
- Not so simple in a solid! All known solutions involve constraining the electrons to be in localized Wannier functions with an extra energy term  $\mathbf{E} \cdot \mathbf{P}$ , where  $\mathbf{P}$  is the macroscopic polarization (Density-Polarization Theory)
- NOTE: in a system with finite polarization in zero field (a ferroelectric), the polarization is determined by the density alone

# Q&A in exact DFT

- Q Can one readily construct different wavefunctions  $\Psi$  that have the same density  $n(\mathbf{r})$ ?
- A Yes. An illuminating example is the homogeneous electron gas. All plane waves have the same uniform density, but only the choice of the lowest kinetic energy states gives the lowest energy ground state for the non-interacting case.
- Q Is it possible to construct an antisymmetric wavefunction for fermions which can describe any possible density (“N-representability”)?
- A Yes, given a few restrictions on the density. It is possible to construct any density integrating to  $N$  total electrons of a given spin from a single Slater determinant of  $N$  one-electron orbitals, subject only the condition that  $n(\mathbf{r}) \geq 0$ , and the integral  $\int |\nabla n(\mathbf{r})^{1/2}|^2$  is finite
- Q Is it possible to generate any such density as the ground state of some local external potential (“V -representability”)?
- A No. A number of “reasonable” looking densities have been shown to be impossible to be the ground state for any  $V$ . One example: linear combination of densities of a set of degenerate states

# Q&A in exact DFT

- Are excitation energies given correctly by the exact density functional theory?
- Yes. In principle, all properties are determined since the entire Hamiltonian is determined.
- Are excitation energies given correctly by minimization of the exact Hohenberg-Kohn or Levy-Lieb functional?
- No. The functional evaluated near the minimum provides no information about excitations, which are associated with saddle points at higher energies.
- Are static susceptibilities given correctly by the ground state functional?
- Yes. All static susceptibilities are second derivatives of ground state energies with respect to external fields.
- Is the exact Fermi surface of a metal given by the exact ground state density functional theory?
- Yes. However, matters are not so simple.
  - First, for the question to be meaningful, the many-body metal must have a well defined Fermi surface
  - Second, it is not a priori obvious that the Fermi surface is a ground state property. However, it can be demonstrated studying the effect of static perturbations to susceptibilities.

# Final remarks on exact DFT

- Although the electron density  $n(\mathbf{r})$  is in principle sufficient to understand all the properties of materials, in practice the relation is subtle and there are no known ways to extract any general set of properties directly from the density: for instance, is a solid is a metal or an insulator!
- Prototypical case:  $N$  non-interacting electrons in an external potential, for which the solution can be found (central problem in the Kohn-Sham approach)
- The exact HK functional is just the kinetic energy, but In order to evaluate the kinetic energy exactly, the only way known is to revert to the usual expression in terms of a set of  $N$  wavefunctions. No way to go directly from the density to the kinetic energy in an exact way.
- This is where Kohn-Sham enters, and how this elegant and so far not very useful theory is changed into one of the most powerful theoretical tools to describe the properties of condensed matter systems.